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Feedstocks, logistics and pre-treatment processes for sustainable lignocellulosic biorefineries: A comprehensive review

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ABSTRACT

More than a century long research and development on utilization of lignocellulosic biomass for biofuels and biomaterials are still in its formative years and the main reason for this is the over-dependence on the fossil fuel reserves. Active research works in the last decades has resulted in a few industrial units to start, stumble and become the forerunners of future biorefineries. But the current system of feedstock logistics and biomass valorization has many drawbacks that make the biorefinery operations unsuccessful throughout the world. This paper discusses the important lignocellulosic feedstocks used, existing and alternate logistical practices, and the pretreatment of biomass for the biorefinery operations. It also emphasises on the importance of decentralized pretreatment of lignocellulosic biomass for the centralized biorefinery operations.

Contents

1. Introduction

Plant biomass captures the solar energy to be used by animals and microorganisms for their energy requirements and biomass production [1]. Human beings have been depending on the lignocellulosic biomass for energy and materials from the pre-historic periods [2,3]. Discovery of petroleum reserves has shifted our dependence on living biomass to the fossilized biomass for energy and materials [4]. Increasing the utilization of biomass to meet the ever escalating demand for energy and materials have been driven by many factors like; over-dependence on fossil reserve of the countries with unstable political situations, increasing fuel prices due to decrease in availability of low cost petroleum reserves [2], attribution of the global warming to the excessive use of fossil fuel reserves, demand for national energy security, and other needs like sustainable and rural developments [5,6]. Higher energy demands of economically developing and highly populated countries like China and India having improved living standards is also a concern to develop renewable energy technologies [7]. The oil problems in the 1970s have had clear effects on the development of biofuel production processes throughout the world [1]. Projects to utilize biomass as a source of fuels and materials are being established at demonstration to industrial scales. These developments have been occurred mainly due to

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the concern on the problems caused by the buildup of atmospheric CO_2 especially from burning the fossil fuels [3].

Even though utilization of biomass for energy and materials has been there from the prehistoric era, the recent question of how to complement or substitute petroleum with biomass as a sustainable source of energy and materials raise many challenges. There is urgency for alternate and sustainable sources for biomaterials and chemicals as most of the industrial chemicals and synthetic materials are produced from fossil resources [8]. Examples of biofuels and biomaterials include but not limited to bioalcohols, biohydrogen, elastomers, fibers, resins, sugars, antibiotics, flavours, dyes, vitamins, polyols, surfactants, oils, dextrins, ethyl ester, organic acids, and solvents. These will be used in industries like transportation, energy, textile, manufacturing, building, cosmetic, pharmaceutical, chemical, plastic, paper, metallurgy, food, wood, pollution treatment, and cleaning [8,9]. The sustainable utilization of biomass requires advanced technologies having high efficiency and throughput. Production of liquid biofuels requires technological inputs that range from the simple extraction of oil from seeds to the production of advanced fuels like higher alcohols and drop-in fuels.

Most of the biomass use occurs in rural areas of developing countries and about half of the world population has been depending on lignocellulosic biomass as their primary energy source. Development of biofuels and biomaterials offers many opportunities for developing countries to have self-reliant energy supplies at national and local levels. It also has potential for providing economic, ecological, social, and security benefits. The performance of biofuels in providing these benefits depends on the type of feedstock and the production process selected [10]. Any drastic change in the existing system of biomass cycle will lead to unintended consequences in nature. Additional effort will be required to maintain the balance in the biomass production–consumption cycle. But, harvesting and utilization of biomass in a sustainable manner does not affect the environment negatively nor leads to carbon imbalance [11].

Value addition of biomass has a lot of scope for scientific, technical and engineering developments. This paper discusses the different feedstock options available for the production of biofuels and biomaterials in a biorefinery concept, the logistic and pretreatment approaches for the lignocellulosic feedstocks for the biorefinery operations. It does emphasize on the concept of decentralized pretreatment of lignocellulosic biomasses for the centralized biorefinery operations.

2. Feedstocks for lignocellulosic biorefinery operations

Lignocellulosic feedstocks for bioenergy and biomaterials production include agricultural and horticultural residues, forest residues, municipal solid waste, live stock manure, perennial grasses, bioenergy crops, aquatic plants, and paper and cotton wastes [6,12]. Selection of feedstocks for biorefinery operations depends on several criteria like potential yield per hectare, adaptation to climate conditions, agricultural inputs required, biomass characteristics, and the potential uses [8]. Even though, many feedstocks have been proposed and studied for biofuel production process their actual potential for market success is not yet proved [13]. The potential feedstocks for biorefinery operations are listed in Table 1. Agricultural residues, fuel woods, and animal dung are already being used as a source of energy in developing countries [14]. These feedstocks can be converted into biofuels and biomaterials through biorefinery technologies. Biorefinery is a conceptual facility similar to the current petroleum refinery where biomass will be converted into fuels, chemicals and energy through process like liquefaction, fractionation, hydrolysis, pyrolysis, gasification, catalysis, and fermentation [15]. Conversion of lignocellulosic residues from agriculture and forestry would significantly supplement the available biofuel produced from starchy feedstocks. Biofuel production using resources having food value are in the centre of the food versus fuel controversy [6], and in many countries biofuel production using food crops failed to achieve commercial success. Feedstock cultivation solely for biofuel production is having many issues such as converting arable lands suitable for food production for fuel production and increasing demand on scarce water resources [6,16]. Cultivation of Jatropha in Myanmar has lead to starvation in rural areas there and the large scale cultivation of single type of feedstock resulted in loss of biodiversity [6] also. These past experiences clearly point out to the need of selecting and cultivating feedstocks that ensure sustainable biorefinery operations [17].

One of the problems with first generation biofuel production was the utilization of starchy feedstocks for fuel production that lead to socio-economic issues in developing countries particularly where the food production was aimed to satisfy the demand for biofuel production in the developed countries. Another concern was the N_2O gas, which is a more potent green house gas than CO_2, released from the agricultural fields excessively supplemented with nitrogen fertilizers for the production of biofuel feedstocks [30]. Similar issues need to be

Table 1
Potential feedstocks for biorefinery operations.

Feedstock	Major producer countries	Estimated global Production (in 2011)	Estimated production in future	References
Rice straw	China, India, Indonesia, Bangladesh, Vietnam	1084 million tons[a]	1267 million tons[a] per year by 2025.	[18–20]
Wheat straw	China, India, Russian Federation, USA, France	1056 million tons[a]	1111 million tons[a] per year by 2025.	[19,21,22]
Sugarcane bagasse	Brazil, India, China, Thailand, Pakistan	502 million tons	666 million tons per year by 2022.	[23,24]
Corn stover	USA, China, Brazil, Argentina, Ukraine	1413 million tons[b]	1639 million tons[b] per year by 2022.	[19,24]
Sorghum stover	India, Nigeria, Mexico, USA, Argentina	81 million tons[a]	108 million tons[a] per year by 2022.	[19,24,25]
Forest wood residues, wood chips and particles	Canada, China, USA, Brazil, Sweden	274 million tons[c]	6 billion tons per year of forest products will be used for bioenergy production in 2050[d].	[19,26–28]
Municipal solid wastes	USA, China, Brazil, Japan, Germany	1.3 billion tons	2.6 billion tons per year by 2025.	[29]

[a] Average straw-to-grain (STG) ratio of 1.5 is used.
[b] Average residue-to-grain ratio of 1.6 is used.
[c] Average wood density of 0.725 kg/m^3 is used.
[d] Data on estimated production is not available.

addressed in the case of lignocellulosic or the second generation biofuel production also, since the production of biomass solely to satisfy the demand for bioenergy production in the developed countries through unsustainable agricultural and logistic practices would lead to socio-economic and ecological problems. The potential to produce biomass without any change in land use, agriculture and forest management practices in the US was estimated to be about 1.3 billion tons annually that can supply energy equivalent to more than 30% of current petroleum consumption [31].

Agricultural residues are by-products of agricultural production and processes, so they do not require additional land, energy, or water to produce them. The cost of agricultural residues is associated with the logistics, handling, transportation, and storage operations. Examples of agricultural residues include; rice straw, rice husk, wheat straw, corn stover, sugar cane bagasse, etc., and they have been used traditionally as animal feed, domestic fuel, and as fuel to run boilers in their respective industries. Sugar cane bagasse and rice husk are being used for co-generation of electricity also and the surplus electricity supplied to the grid [32]. The horticultural residues like fronds, empty fruit bunch, trunks, shell and fibers of palm are available in countries like Indonesia and Malaysia. Residues from sugarcane, coconut and rice cultivation and processing are available in Philippines, Thailand, Indonesia, and Vietnam [17]. Chinese annual production of agricultural residues in 2007 was estimated as 752 million tons and about half of it could be used as resources for the production of fuels and chemicals. Efficient utilization of agro-residues is limited in China as only 0.5% is being used for biogas production, 23% as forage, 4% for industrial use, 37% is used for combustion by farmers, and the remaining 35.5% wasted during collection and left in the field to decay or burnt [33]. It has been shown that, use of crop residues in biorefinery systems reduces green house gas emissions by about 50% and fossil energy demand by 80% [34].

The agricultural and horticultural residues available for industrial conversion will be significantly less than the actual quantity available in the field. In totally dry weather conditions these residues should remain in the field to prevent excessive evaporation and in other conditions most of it should be recycled to the soil as nutrients and to prevent soil erosion. Some quantities of residues will be used as cattle feed and for other traditional uses like roofing and heat production [12]. The actual quantity of agricultural and horticultural residues is also influenced by the available technologies for the recovery of it from different stages of crop processing. After considering all these factors the agricultural residues available for biorefinery operations would be about 15 to 40% of the total residues produced [35]. The appropriate post harvest technology is essential for maximizing its use.

Many studies have considered the large scale monoculture of biofuel crops as a means for the economic viability of industrial production of liquid biofuels. Sugar cane has been used for commercial ethanol production in countries like Brazil which is a practical example of industrial production of biofuels using non-food crops [36]. In Western Europe, short-rotation coppice crops like poplar and willow have been cultivated to produce biofuel and similarly, in Northern America and Europe, miscanthus has been promoted as a bioenergy crop. Some countries in Asia and South America have indigenous bamboo species that can be used for biofuel production as they require minimum agricultural inputs. Eucalyptus trees can be cultivated in salty areas to restore the land for future cereal production [37]. Other sources of similar type of first generation biofuels is ethanol produced from starchy sources like corn and wheat. But, the sustainability of this first generation especially the grain based biofuel production is not yet proved. The problems like poor energy balance, impacts on regional water sources, biodiversity, and soil quality are associated with it. Monoculture of bioenergy crops would aggravate problems like soil erosion, pollution from nutrient leaching and overdraft of underground water. Sugar cane cultivation is associated with high levels of soil erosion and because of its monoculture nature this leads to greater loss of biodiversity as well [15,38].

Forestry residues like chips, saw dust, particles and unused woods produced during the forest harvest and wood processing are also available for biorefinery operations. Forestry and agricultural resources and their residues are greatly available in Southeast Asia. It is estimated, through the national forestry survey (1999–2003), that a total of about 2.45 billion tons of forest residues are produced each year in China [33]. It includes about 11 million tons of forest wood residues and 17 million tons of wood chips and particles in 2003 [19]. These residues are often causing pollution problems as the prevalent practice is to burn them openly or using it to generate steam. Open burning of high moisture containing biomass will produce green house gases and particulate matters that are detrimental to life in those regions [17]. The forest residue removal should be in harmony with the local ecosystems and be practiced under the sustainable forest management. Large quantities of wood for biorefinery operations would be available during the outbreaks of infection and diseases to the woods [35]. Forest management practises for wildfire control combined with the local energy production using wood residue would provide benefits like protecting people from rising energy costs, reduced dependence on fossil fuels and carbon emissions, and self-sufficiency for energy and materials [39].

Aquatic plants like algae are considered as the source for third generation biofuels, it can produce 30 times more fuel than terrestrial lignocellulosic crops. It can be cultivated in brackish and waste waters, and they can be fed with CO_2 [6] or NO and is a solution to address the issue of increasing concentration of these green house gases in the atmosphere. The oil from algae can be processed similar to the first generation seed oil and the technologies for it are being developed. Use of algae in biorefineries is still in its infancy and scientists are working to develop methods to handle and use them industrially and efficiently. High-yielding strains have to be developed, the culturing methods and media have to be optimized, sustainable commercial plants are needed to be designed with due consideration to environment [37].

Municipal solid wastes (MSW) are another important resource and the main components for biorefinery operations are paper, cotton, and garden and kitchen wastes. MSW generation and thereby its availability increases every year in both non-industrialized and industrialized countries alike. The biomass produced in urban and peri-urban areas for the greening [40] and food production [41] will also be contributed to the production of biofuels and biomaterials [42,43]. The estimated annual production of MSW in India for 2011 was 80 million tons with per capita increase of about 1.33% per annum due to population growth and economic development. Paper sludge is another resource produced in pulp and paper industries which can be used in biorefineries for the production of biofuels and biomaterials. Paper sludge availability may be limited and also contain heavy metals in it that needs further work to integrate this resource with other feedstocks and also in developing methods to remove the fermentation inhibitory materials from it [32]. China produced 2.48 billion tons of animal manure and 152 million tons of municipal solid waste (MSW), 1756 million tons of industrial solid waste, 24.66 billion tons of industrial waste water and 31.02 billion tons of municipal waste water in 2007. Based on the availability of different biomass resources, the potential bioenergy production capacity in China was estimated to 20.68×10^8 tce (tons of standard coal equivalents) and the acquirable quantity was 4.89×10^8 tce in 2007 [33]. The main drawbacks of MSW as a source for biorefinery operations include the variation in composition of it from place to place and the question of whether the transportation fuels derived from it be considered as biofuels or

not since MSW contains inorganic materials like plastics and metals in it [44].

Green biomass available from urban areas is an important and underutilized resource for bioenergy and biomaterials production [45]. The biomass like the lawn thatches and cuttings, grass, leaves and twigs from the gardens, green roofs, and recreational parks contributes to the estimated 164 Mg of dry biomass which can be collected from the planted urban areas in the USA [46]. The total area under the green cover has been increasing in cities around the world due to the environmental and esthetic concerns. The garden waste available from cities in China has the potential to produce biofuels containing 260 quadrillion joules of energy that can reduce the carbon emissions from the urban areas [47]. Utilization of biomass from urban areas requires further research and development works to overcome the constraints related to variation in quality and availability of biomass, and technological implementation [48].

Sweet sorghum is a sugar feedstock for bioenergy production and is gaining momentum for its cultivation in different parts of the world. It has high photosynthetic efficiency, high stress tolerance, less fertilizer requirement, rapid growth rate, ease of planting, wide adaptability and produces more ethanol per unit area than corn. Sweet sorghum produces grains which can be used for food production, fodder which can be used as cattle feed, sugary juice which can be fermented to produce fuel ethanol [33], and the bagasse remaining after extraction of juice can be used for biorefinery operations to produce fuels and chemicals. Improving the productivity of sorghum varieties through genetic engineering, plant breeding and other advanced methods is well undertaken by researchers in both developed and developing countries. Researchers in China have increased the sugar content in stem of sweet sorghum through hybridization, ion beam irradiation, and genetic engineering to increase its productivity. Similarly, the *space flight mutation breeding* of sweet sorghum has also been conducted for increased stem sugar content and juice preservation period with decreased size of the plants. The cultivation of sweet sorghum increased in China and ethanol production from the juice has been demonstrated at plants of size 3000–5000 t per annum in provinces like Jiangsu and Heilongjiang. Fuel ethanol production has been demonstrated using about 50,000 ac of sweet sorghum cultivation in Shandong province. These plants were utilizing solid state fermentation technologies while a pilot plant in Baiyin, Gansu province was utilizing technologies for the direct fermentation of sweet sorghum juice for ethanol production [36]. Sorghum is produced in 12 million hectares in India, the second largest producer of sorghum in the world, producing 10 to 11 million tons of sorghum per year. The first commercial scale production of ethanol from sweet sorghum in India was established at Nanded, Maharashtra in 2007 with a production capacity of 7000 t/year [49,50].

Sweet sorghum can be cultivated in areas where sugar cane cultivation is not feasible [38]. Studies have shown that sweet and forage sorghums can be cultivated industrially to meet the demand for second generation biofuels in a sustainable manner and the existing infrastructure can be used for it. The nitrogen and water inputs for the cultivation of many sorghum varieties are less than that for other bioenergy crops. Farmers can cultivate sorghum as an annual crop rather than as a perennial crop that would take the lands for decades [51]. Even though, perennial crops would result in higher environmental benefits than annual crops [52], farmers would be reluctant to long-term commitments of land and resources by cultivating perennial bioenergy crops like miscanthus, switchgrass, and coppice trees, unless they are convinced with clear positive market signals and adequate financial security [13,53].

Lignocellulosic materials can contribute considerably to the energy and chemical demands of the world. More dedicated feedstock should be produced to significantly increase the contribution from the lignocellulosic conversions. Additional biomass production for biorefinery operations needs to be cautioned for the chances of deforestation and similar unsustainable practices including farming priority to fuel over food. The biorefinery operations should ensure the uninterrupted supply of raw materials by utilizing diverse feedstocks, because biomass production is susceptible to multitude of factors including ecological, economic, and biological factors such as pest infestation, draught, and fire. The combination of different renewable and non-renewable energy options with sustainable development practices would ensure the energy security of each country of this planet [35].

3. Logistic practices for biorefinery operations

Logistic practices for biorefinery operations include a number of harvesting processes, storage of the harvested biomass, pretreatment, and transport of the processed biomass [54]. The prevalent biomass logistics for biorefinery operations is shown in Fig. 1. Transporting the feedstock from the source to the final processing centre contribute to the major cost of the logistics [55]. The estimated daily biomass requirement for an economical biorefinery operation is 5000–10,000 MT. This volume of feedstock requirement would increase the cost of its transportation and storage, and create local environmental issues [5]. Economical handling of agricultural residues, forest resources, and municipal solid wastes for biorefinery operations requires; improved biomass production, improved equipment throughput capacity, reduced dry matter losses at each stages of handling and storage, efficient strategies for handling of high moisture content biomass, supply of biomass in desired quality and format, strategies to reduce the infrastructural and social effects of increased transportation, secured health and safety conditions of workers and the communities involved in the system, and accurate standards based on life cycle analyses. Livestock manure from farms

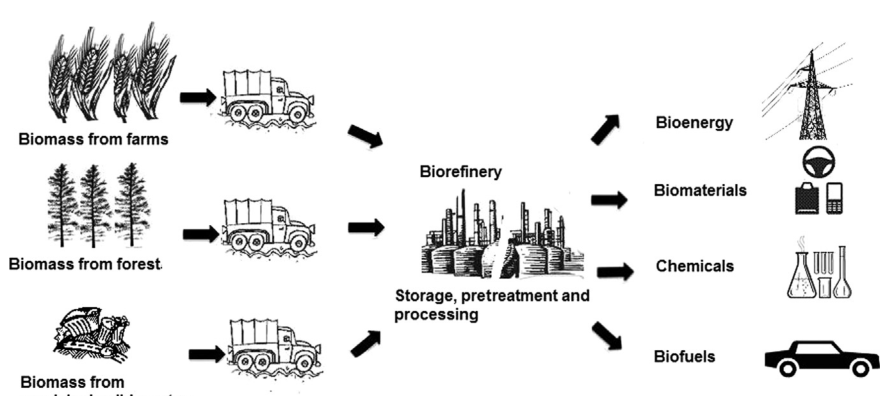

Fig. 1. Prevalent biomass logistics for biorefinery operations.

can be collected through cooperatives or networks after developing sustainable storage guidelines and facilities. There should be systems to remove the moisture content in the manure and the transportation costs should be reduced. Using algae and other aquatic plants for biorefinery operations require the development of efficient systems for dewatering, oil extraction, drying, and storage of the feedstock [56]. All these steps are part of the post harvest technology of energy crops.

One of the main barriers to the establishment of successful biorefineries is the lack of sustainable supply chain for lignocellulosic feedstocks [57]. Economical biofuel production by the biorefineries requires the supply of feedstocks having consistent quality, particle size, and moisture content. Production and supply of feedstocks with consistent quality have greater market potential. The high moisture content and low energy and physical densities of biomass make their collection, handling, transport, storage and processing uneconomical in the current biofuel production scenario. The equipments used for harvesting and transport of lignocellulosic feedstock needs improvement in their efficiency and reduction in cost through research and development. The technologies which are currently being used to preprocess lignocellulosic biomass are expensive, inefficient, and add significantly no value to the raw materials. These technologies also release air pollutants and green house gases; hence improvements in this area would help in reducing or avoiding the fossil fuel use to produce, harvest, and handling of lignocellulosic biomass. Biomass production should be sustainable that maintains the organic content and productivity of soil with prevention of soil erosion. Developing an efficient biomass logistic system will provide significant socio-economic benefits to rural communities by creating multitude of job opportunities like; production, harvest, preprocess and transport of feedstock for biorefineries, sale, and maintenance and service of equipments for biomass logistics. Biomass preprocessing to supply the feedstock materials at specific quality and format is important and it requires research to develop such processes applicable to on-farm conditions. Simple preprocessing technologies for size reduction and densification to physical breakdown can be applied on-farm to add value to the biomass. Improved systems and machineries for the efficient transport of processed materials need to be developed. Industry should involve in developing the sustainable logistic system for biorefinery operations through actively participating and supporting the research and development domain of preprocessing and efficient handling of lignocellulosic feedstocks [56].

It is expected that the supply chain for biorefinery operations would increase the transportation volume in the near future and it is an opportunity for transportation and the associated manufacturing industries; although these additional transportation volume will exert greater amount stress not only on society but also on environment. This increased demand for biomass could promote development of rural infrastructure for transportation, manufacture and biomass processing. It would also enhance agriculture and provide the associated economic development in both developed and developing countries. The environmental impacts of these operations will depend on the way it is designed and implemented. Moreover, the respective policies of the government will determine the ultimate effect of new bioeconomy on agriculture, environment and energy [58]. Research and development is required to meet the societal goals of sustainable biomass logistics. Simulation models and commercial demonstrations should be adapted to local feedstocks, technologies, infrastructure, and socioeconomic conditions [59].

4. Pretreatment options for liquid biofuels and biomaterials from lignocellulosics

The history of pretreatment of lignocellulosic biomass for biofuel production started a century ago with treatments using acid and steam. Systems for biomass fractionation have been developed in the 1920s, based on acid hydrolysis and steam explosion and recently many other solvents and chemicals have been used as catalyst for the pretreatment. The research into pretreatment technologies has been getting increased attention in recent times as it is one of the main bottle necks for the commercial production of cellulosic biofuels. Many pretreatment processes have been developed in the last decades and are being continuously improved through research studies [2]. The pretreatment process has significant effects on all downstream processes and ultimately influence the overall biofuel yield and cost [31]. Even though many pretreatment processes have been developed so far, there is not a single ‘perfect’ pretreatment process or the “best technology pathway” available for all types of lignocellulosic feedstock and end products [15,30]. But there are some properties required for a pretreatment process to be considered as industrially viable; the pretreatment process should result in maximum recovery with minimum degradation of the components, minimum capital and operating costs, applicability to a large variety of feedstocks available, and minimum requirement of further treatment processes prior to end product formation [2,60].

Lignocellulosic biomass pretreatment processes will be having an aspect of biological, chemical, and physical reactions in each of them, so only a combinatorial classification of them will be feasible. Mass balance is the primary parameter to characterise the efficacy of a pretreatment process. It will be followed by the economic analysis taking into consideration the up-stream and down-stream processes. Physical process such as comminution is applied at different stages of pretreatment. It will increase the surface area of the substrate to increase the reaction rate, and decrease the degree of polymerisation and cellulose crystallinity. It is a highly energy intensive process and the final particle size ranges from 0.4 to 50 mm depending on the process requirements and characteristics. Fractionation techniques are being studied and developed for the isolation of the base components such as cellulose, hemicellulose and lignin to facilitate the industrial conversion of them separately. In the sequential pretreatment of lignocellulosic biomass, each of its components will be isolated separately through consecutive treatment processes [35].

Chemical pretreatment is applied through the use of chemicals like alkalis (NaOH, $Ca(OH)_2$, KOH, hydrazine, NH_3), acids (H_2SO_4, HCl, H_3PO_4, organic acids), organic solvents, and ionic liquids [31]. They are the most widely studied lignocellulosic biomass pretreatment techniques having most of the required characteristics of an industrial process. Examples for the chemical pretreatments are Ammonia fiber expansion (AFEX), super critical fluid pretreatments, ionic liquid pretreatment, acid hydrolysis, alkaline hydrolysis, and organosolv pretreatment (OP) [31].

Acid pretreatment processes use either concentrated or dilute acids to hydrolyse the carbohydrate polymers in the lignocellulosic biomass. Hemicellulose and lignin would be solubilised during acid pretreatments and the use of concentrated acid would hydrolyse cellulose also. Acid treatment will result in other high value products like furfural, hydroxyl-methyl furfural (HMF), phenolics, aldehydes, and aliphatic compounds [30]. These products have to be removed before subjecting the residues for further biochemical treatments. Acid pretreatment processes using mineral acids require corrosion free reactors [32] and more over neutralization and detoxification process are also necessary [31,61].

One of the oldest and most widely studied biomass pretreatment methods is the treatment using water at high temperature and pressure [30]. The pretreatments using water at high temperature are called autohydrolysis and steam explosion. Steam explosion treatments use both physical and chemical reactions to disrupt the structure of lignocellulosic materials. In these treatments, the substrate will be subjected to high pressures and temperatures for short duration of retention times followed by the rapid release of the elevated pressures to atmospheric pressure

which will break the polymeric bonds in the substrate. The acidic conditions produced with the liberation of acetic acid from hemicellulose and action of water as an acid at higher temperatures facilitates the hydrolysis reactions [31]. The effectiveness of this process depends on particle size, and it has been observed that relatively larger sized particles produce higher sugar concentrations than from fine particles. The temperatures applied will be in the range of 190 to 270 °C and the residence time will be reduced with increase in temperature and it varies from 1 to 10 min. The increased pressure will be a function of higher temperature applied to biomass slurry containing water. Two-step steam explosion also has been studied to increase the ethanol yield and are found to be promising for further studies and development to decrease the higher energy inputs. In two-step steam explosion first treatment will be applied to extract the hemicellulose followed by the second one to break the carbohydrate bonds in the cellulose. Acid catalysis also studied within the steam explosion treatment and is found to reduce the temperature and retention time with decrease in formation of unwanted products and complete hydrolysis of hemicellulose. But, addition of dilute acids also demands the neutralization of the different product streams before further processing. In liquid hot water (LHW) treatment biomass [4] will be subjected to higher temperature (180–230 °C) and steam pressures [30] but the release of the elevated pressure will be slower than in steam explosion treatment. The main advantage of LHW treatment over steam explosion treatment is that, it requires less expensive reactors [61].

In biochemical biorefining, lignocellulosic biomass is disintegrated initially into its multiple components for separate conversions in succeeding stages of the production processes. Biotechnology has a major role in biochemical conversion processes which is preferred over thermo-chemical conversion processes for their selectivity. But, the complex lignocellulosic biomass resources require multiple processes for their fractionation and value addition to the components. Moreover, biological processes are slower and require higher operation areas than for thermo-chemical processes [62]. Biological pretreatments using fungi and bacteria takes long time to achieve the required reduction in degree of polymerisation but are specific and efficient. The treatment time for biological treatment varies from 10 to 14 days at controlled atmospheric conditions and in very large spaces. Some fractions of the substrate will be consumed by the microorganisms for their growth. All these make direct biological pretreatment processes less favourable for industrial applications [2,31]. But, many upcoming bioenergy companies are applying the enzymatic hydrolysis and microbial fermentation for biofuel production [63–67]. The advantages of industrial enzymes include high product specificity, faster conversion of the substrate, low energy requirement due to mild processing conditions, minimum environmental problems, and the recent reduction in cost of enzymes for biomass processing [68,69].

Ammonia has been studied as an excellent reagent for the pretreatment of lignocellulosic biomass and the results lead to examples of pretreatment processes using ammonia which include ammonia fiber expansion (AFEX), ammonia recycle percolation (ARP), soaking in aqueous ammonia (SAA), and ammonia hydrogen peroxide treatment. Ammonia fiber expansion (AFEX) is much like steam explosion treatment in which biomass will be subjected to higher pressures using concentrated ammonia and the pressure rapidly released to break the bonds between the polymers in the substrate. Important advantages of AFEX treatment include low moisture content, lower formation of sugar degradation products due to lower temperature requirements, and complete recovery of solid material [31]. The disadvantages of AFEX treatment include the cost for recovery of the reagent and the safety concerns [61]. Ammonia recycle percolation (ARP) process is similar to the LHW treatment where liquid ammonia at 5–15% concentration passed through the packed bed of biomass at higher temperatures of about 140 to 210 °C. But, ARP has all the disadvantages of AFEX process and it needs to be studied and developed further to reach the industrial level of operations [61].

Supercritical fluid pretreatment (SCP) uses gases or liquids at their supercritical conditions to increase the solubility of lignocellulosic materials. At supercritical conditions reactants will be having higher diffusivity and there by overcoming the mass transfer limitations in other pretreatments. Supercritical CO_2 and supercritical water treatments have been studied and are found to be with excellent potential for lignocellulosic biomass pretreatment. The higher pressure requirement, which is about 200 bar, makes this treatment uneconomical for industrial level of biomass pretreatment [61].

Alkaline pretreatment using bases causes the bond breaks in ester and glycosidic side chains that lead to partial structural changes in lignin, cellulose, and hemicellulose. The conditions for alkaline pretreatment is less severe compared to other chemical pretreatments, but longer treatment time is the drawback of these treatment processes. Lime pretreatment is one of the low cost biomass treatment processes, and the recovery of lime can be achieved by using CO_2. Recent studies have incorporated advanced technologies like radiofrequency, microwave to the alkaline pretreatment and have shown to be enhancing the biomass hydrolysis through uniform heating and an explosion effect among biomass particles [61].

Ionic liquids (IL) or the green solvents are gaining importance in lignocellulosic biomass pretreatment as IL can dissolve a wide variety of substrate types. Ionic liquids have low vapour pressure and are salts which exist as liquid at room temperatures. They are composed of a small anion and an organic cation and the type of ion varies depending on ionic liquid selected. Ionic liquids are recoverable after the pretreatment and no toxic products are formed after the treatment process, but presence of IL on treated samples inactivates cellulase during enzymatic hydrolysis. The treatment involves the dissolution of the biomass in IL and precipitation of the individual component using water. IL treatment does not significantly alter the structure of individual polymers in lignocellulosic biomass [70]. The main drawback of IL treatment is the cost of ionic salts and its synthesis at large scale would help to reduce its cost [61].

Organosolv pretreatment (OP) uses organic or aqueous-organic solvent with or without a catalyst to delignify lignocellulosic materials. Catalysts used include inorganic acids like hydrochloric acid (HCl), and sulphuric acid (H_2SO_4), and organic acids like oxalic acid, acetylsalicylic acid, and salicylic acids. The main organic solvents used include ethanol, methanol, ethylene glycol, glycerol, ethers, phenols, and ketones. The main advantage of OP is the selective extraction and is effective for high lignin containing biomass. It can be combined with other lignocellulosic biomass pretreatment processes to improve the efficiency of them. Disadvantages of OP are the high cost of solvents and reactors and the degradation products formed due to acidic catalysts [2].

Thermo-chemical biomass conversion processes, which are mainly under development, for the production of biofuels, energy and biomaterials include pyrolysis, gasification and liquefaction. These technologies convert biomass into gaseous and liquid fuels, electricity, heat, and chemicals. Pyrolysis occurs when heat is applied to a material in the absence of oxygen. The products of pyrolysis of biomass are bio-oil, biochar and syngas. Bio-oil is a mixture of aliphatic and aromatic chemical compounds like alcohols, aldehydes, acids, sugars, esters, ketones, phenolics, hydrocarbons, oxygenates, etc. Liquefaction is the heating of biomass in presence of a catalyst to produce a heavy oil product containing hydrocarbons that can be directly used as a fuel [15]. Thermochemical pretreatment processes are found to be the most suitable for future biorefinery operations. Different aspects of technical, economical, and ecological parameters

should be critically analysed before adapting these technologies for the biorefinery [31].

Catalytic conversion is one of the critical and controlling technologies in biorefinery operations [71]. There are some barriers to the development and implementation of catalytic technology and they include economic barriers, selectivity of catalysts for particular substrates to products, and design, operation and control of catalytic reactor. Selection of catalyst is important as it determines the product formation efficiency. Catalyst technology also has to be combined with suitable separation technology for the products. Nickel-based catalysts, like nickel–alumina or nickel–silica, have been used to increase the yield and quality of bio-oil from biomass through pyrolysis [72]. Chlorides, carbonates, and chromates are also found with catalytic properties to improve biomass pyrolysis. Some of these catalysts are also used for the production of hydrogen from organic compounds in bio-oil through catalytic steam reforming followed by a water–gas-shift reaction. Noble metals like platinum (Pt), rhodium (Rh), and rubidium (Rb) are found as excellent catalysts for the hydrogen production from bio-oil, but are too expensive to use industrially. Cobalt and molybdenum metals and their oxides are also used as catalysts for upgrading bio-oil to hydrogen or carbon monoxide [71].

Biomass gasification is the process of converting biomass into syngas which contains hydrogen, carbon monoxide, carbon dioxide, and methane by applying high temperature (more than 720 °C) in the presence of oxygen. Biomass will be converted into syngas and charcoal and the syngas can be converted into hydrogen through steam reforming and water–gas-shift reactions. Fischer–Tropsch synthesis is applied to convert the syngas into long chain hydrocarbons, drop-in fuels, wax and naphtha using catalysts like cobalt (Co) or iron (Fe) [73]. One of the advantages of gasification-catalytic conversion route is that, it can convert the whole biomass including lignin into fuels and chemicals and it does not require the energy intensive product separation as in biochemical routes. Further research is required to achieve efficient heat and mass transfer with integration of individual processes effectively [71]. There are some attempts to produce cellulosic ethanol at commercial scales through biomass gasification and catalytic conversion processes [30,32]. Similarly, black liquor gasification is being developed to significantly reduce CO_2 emissions and also to recover energy and chemicals at biomass pulp mills [74].

Torrefaction of lignocellulosic biomass is also being studied as a pretreatment method to overcome the issues associated with the low density of biomass. In torrefaction treatment, biomass will be subjected to mild pyrolysis conditions of 200–300 °C under inert condition. The resulting torrefied biomass will be higher in physical and energy densities and lower in impurities in it [75]. It may be less susceptible to the fungal attack as it contains minimum amount of moisture. Torrefaction can overcome the inherent issues like heterogeneous nature in terms of physical, chemical and morphological properties. But, the complexity and variety of the feedstocks are so high that this technology requires further study and development to understand the exact parameters with respect to the polymeric structure and mineral composition of biomass. The by-product streams of the solid product also need to be studied and utilized to improve the efficiency of the process [76].

Biomass-to-liquids (BTL) technologies are available for the conversion of biomass to drop-in fuels. BTL technologies are adapted from the coal-to-liquid (CTL) and gas-to-liquid (GTL) technologies. The studies have shown that large-scale BTL technologies would be economical when the crude oil price increases and the environmental aspects are considered. The existing systems for CTL and GTL technologies are highly energy intensive as they require biomass to be fine powdered to the micron sized particles for gasification. Large-scale BTL technologies have issues with the transport of feedstocks with low energy density. Pre-conversion processes are an option to increase the energy density, ease of transportation and handling of the feedstock. The distributed pyrolysis of the feedstock as a pre-conversion process (PCP) to produce bio-oil or bio-slurry for large-scale BTL application is found to be economical [77].

While considering all of the above processes described, it is not possible at present to conclude which biomass valorization process would be techno-economically efficient and sustainable. The potential processes for the decentralized pretreatment of lignocellulosic biomass are given in Table 2. It is likely that, there would be different processes suitable for different feedstocks depending on the composition of the feedstock and the end products. So, a holistic examination is required with each feedstock at different places to select a particular biorefining process for it [30].

Biorefinery is being holistically defined as “an integrated pattern of farming and conversion activities capable to provide bioenergy and biomaterials as alternative to fossil-based refineries, increasing job and income in rural areas” [84]. Biorefineries can be classified into green biorefinery [85], forest and lignocellulosic based biorefinery, aquatic or algae based biorefinery, and integrated biorefinery. The green biorefinery primarily uses starch and sugar materials like cereals, tubers, sugar cane etc., along with terrestrial wet biomass such as green plants, grasses, and silage [85], and bioenergy crops to produce biofuels and biomaterials through primarily biochemical processes. In this biorefinery, first the feedstocks will be pressed to extract the green juice which contains proteins, amino acids, dyes, pigments, and other organic substances and minerals [85]. Then, the remaining fiber rich fraction will be fed into the lignocellulosic biorefinery for the production of biofuels and biomaterials through biochemical and thermochemical processes. The forest and lignocellulosic based biorefinery uses the three main components of plant biomass; cellulose, hemicellulose and lignin to produce biofuels and biomaterials. In lignocellulosic biorefinery theromochemical processes

Table 2
Potential processes for decentralized pretreatment of lignocellulosic biomass.

Process	Main Catalyst	Temperature (°C)	Time	Catalyst (g): Biomass (g)	Solid (g): Liquid (g)	Comments	References
Lime	$Ca(OH)_2$	100	60 min.	1:10	1:10	Comparatively safe and low cost process.	[78]
Liquid Hot Water	H_2O	160–230	10–20 min.	10:1	1:10	High temperature requirement is an issue.	[79,80]
Biological	Microbes or Enzymes	30–50	1–28 days	1:10	1:4	Very slow process and requires sterile conditions.	[81]
Soaking in Aqueous Ammonia	NH_3 or NH_4OH	60	12 h	1:1	1:6	NH_3 recovery and safety of the workers are the issues.	[82]
Dilute acid	H_2SO_4 or HCl or HNO_3 or H_3PO_4	120–190	20–60 min.	1:10	1:10	Acid resistant construction materials are required.	[83]

like pyrolysis, gasification, combustion, liquefaction, hydrolysis, catalytic conversion, and fermentation are applied separately or in combination to treat the feedstocks. Fractionation of lignocellulosic biomass to its main components has been studied by researchers and this fractionating unit is considered as the centre of the biorefinery and it is required to be efficient, economical, robust, and reliable. Reagent recycling and use of simple reaction vessels are required to improve the economics [70,86].

Aquatic or algae based biorefinery uses algae as feedstock for the production of biodiesel, biohydrogen, biopolymers, proteins, amino acids, polysaccharides, pigments, animal feeds, biofertilizer, etc. Algae based biorefinery has high potential to capture the CO_2 emitted from fossil fuel burning industries, and utilizing nutrients in agricultural runoff, industrial and municipal waste water. Algae can be grown in brackish and saline water bodies and also in photo-bioreactors set up at desert and arid lands. The integrated biorefinery is the amalgamation of other types of biorefineries and will be having facilities to handle all types of feedstocks and produce all types of biofuels and biomaterials [87].

Life cycle analysis studies show biorefinery operations to have higher eutrophication potential than the petroleum based refinery. This aspect should be taken into consideration to find an appropriate mitigation measures while establishing biorefinery projects. Even though the assessment of different aspects of biorefinery operations is complex due to the uncertainties associated with it, production of fuels and chemicals from agro-residues shows reduction amounting to 50% in GHG emissions and 80% in non-renewable energy use. The results will vary depending on the feedstocks, conversion routes, products and their applications, and the assessment methods [34].

Technology Roadmaps (TRM) for biorefinery development [88] would help in bringing consensus among different stakeholders to create a common vision, goals and targets. TRM is a flexible and powerful tool for planning strategies to integrate technology and business in a sustainable manner. It would develop guidelines for policy and decision makers, market research to find gaps and barriers, finding and assessing technology alternatives and strategies to overcome the gaps and barriers, and above all it would improve the communication and coordination of renewable energy technology development. It is imperative to review and update the TRM regularly to address the timely developments in technology and society [7].

5. Status quo of lignocellulosic biofuels and biomaterials production

There are some initial studies on the feasibility of large scale production of biofuels to meet the increasing energy demand and also to replace the use of fossil fuels [38,58]. A few of the earlier studies are not advising in favour of large scale production of biofuels [16,38] and it is considered to be impractical to replace the current petroleum consumption with biomass in a significant manner [35]. These studies have shown that, most of the countries do not have the land, water and labour required for the production of large quantities of biofuels [38]. The demand to supply ratio of land required for biofuel production varies from 1.4 to 148 and the ratio for fresh water demand and water withdrawal is 3 to 104, and 20 to 40% of the existing work force also will be required for the biofuel production. There will be additional demand for resources to meet the environmental parameters of these technologies [38]. Heavy reliance on biofuel production without the consideration of environmental factors would result in serious impacts in comparison to the use of fossil reserves [89]. Increasing the efficiency of agricultural production is also not found to be ensuring the energy security through biomass production for biofuel [38]. Studies have also shown that, the estimated total work force required for the biofuel industry is less than 1% of the available work force of the nation [58], and the new jobs available in the current mode of biofuel production will be 13 times less than that of new jobs created with the expansion of pulp and paper industry [35]. These facts are indicating that the current approach towards biofuel production has to be strategically improved to make it more sustainable and has potential in providing more job opportunities.

There are technological, economical, logistic, safety and policy barriers to the development of lignocellulosic biofuels around the world. The technical and non-technical problems hindering the development and commercial success of biorefineries include the high cost of production, harvesting, storing and transport of biomass for biorefinery operations. The annual crops used for biofuel and biomaterials production should be harvested in a short time period and stored for the rest of the year. Production costs include the usual agricultural inputs like nutrients, pest and decease removal, and irrigation. Land utilization for specific bioenergy crop production in a monoculture method leads to significantly negative ecological and social side effects [15].

Production of second generation biofuels is elusive in terms of commercial production and is considered as the products for the future [32]. First generation biofuels are being produced from starch and sugar crops while the second generation biofuels are produced mainly from lignocellulosic biomass. The time estimated for the start of commercial level production varies depending on the investments from the private sector and also on oil prices. Based on these factors, as of 2010, it was estimated that it would take more than five years to begin the commercial level production of lignocellulosic biofuels [6]. The studies have also shown that second generation biofuel production will overtake the first generation biofuel production, which is already in commercial levels of production, within 10 years. The second generation biofuel industry will be developed based on the knowledge and experience acquired through the commercial level production of first generation biofuels like bioethanol using starch and sugar feedstocks and biodiesel using plant oils. Similarly, synthetic biofuels based on the Fischer–Tropsch process is expected to be available in the market by 2020 [17].

The ever increasing demand for energy and the accompanied increase in oil prices have prompted both developing and developed countries to utilize the potential of the domestic alternate resources for energy. Developing countries like Brazil and many developed countries in Europe and America are in the forefront of alternate energy production. Asian countries also have significant potential to produce biofuels using wasted crops and crop residues such as rice straw, wheat straw and maize stover [16]. Biofuels can play an important role in the development of African countries as more than forty two of them are facing difficulty in providing good and adequate supply of energy services. But, development of biofuels like bioethanol and biodiesel in Africa has become a controversial issue due to the land use change and deforestation [10]. Many African countries are having arable and fertile lands for the sustainable production of energy crops and countries like Togo, Niger, Mozambique and Ghana are having thousands of hectares of Jatropha farms for the production of biodiesel [10]. Many other areas of Africa are also considered as having potential to produce biomass feedstocks by international investors. But, only a few countries like South Africa, Mozambique, and Tanzania are having government policies for the development of biofuels for their own use. In many countries biofuel projects have lead to 'land grab' issues between the investors and the local people [16].

Developing countries have a positive outlook towards the development and use of renewable energy technologies [90]. Bioenergy accounts for about 38% of the primary energy consumed

in developing countries [1]. Moreover, use of biofuels in the transportation is mandatory in many of the developing countries. In order to meet the demand for biofuels for the blending purposes, the lignocellulosic biomass should be utilized for the production of biofuels. But, availability of lignocellulosic resources for biofuel production is poorly documented in developing countries like India. The technologies for lignocellulosic biofuel production are under development and well planned research is required in this field [91].

Resources such as agricultural residues, wood and grasses are being used by a large number of people in the developing countries for their livelihood [92], and utilization of these materials would demand the compensation and/or alternate livelihood options for them. Like in any project involving multiple stakeholders, biorefinery operations also encourages the continuous and mutual learning with active participation by all people including local farmers and industry owners. Capacity building is required at all levels with innovations that address the local needs, and the local development accompanied with the biorefinery operations would be realized by the rural people involved [93].

There are many issues with the application of second generation biofuels in developing countries. The technologies are mainly developed and applied in industrialized countries and they are characterised by high capital and energy investment, aimed to minimize labour and maximize resource utilization and product formation, and are developed for feedstocks which are alien to most of the developing countries. Developing countries have to adapt those technologies to reduce capital investment per unit, increase people participation and modified for native feedstocks available [6].

Biofuel production in Southeast Asia has is not on track yet because of the lack of adequate scientific understanding and directions. The region should have its own roadmap considering the climatic and geographical conditions for the successful implementation of the biofuel production process from the lignocellulosic residues. Technological understanding through research and development and strong support and funding from government is also required to make economical production of biofuels a reality. Efficient utilization of the agricultural residues requires building up of a logistic network for the collection and processing of it. In comparison with first generation biofuel production second generation biofuel production is more promising and less risky in nature. From alternate analyses, it is clear that second generation biofuel production can be used for the development of rural areas especially in the developing countries. But, relevant strategies have to be planned for the connection between the biomass feedstock producers in the rural areas and the biorefinery authorities [17]. Policy issues become crucial in making solid progress in this area.

Non-food agricultural produces like sweet sorghum, tuberous crops, cellulosic biomass, and algae are available in China for the production of biofuels. China has the rules to regulate biofuel production to avoid competition with the prevailing agricultural system and land used for food production [36]. Taiwan is targeted to produce about 300 million litres of bioethanol and 15 million litres of biodiesel by 2020 [94].

European Union (EU) has resources available for the production of bioenergy and studies have identified the economic conditions, industrial know-how, institutional capacity and the co-ordination of the supply chain as the key barriers to the successful implementation of bioenergy projects. These barriers are mainly non-technical rather than technical and there are coherent strategies and interventions to overcome these barriers [95]. The supply chain co-ordination between the farmers and the companies requires prime effort in the establishment of any bioenergy project. The combined heat and power (CHP) project in Enköping, Sweden using salix plantations is an example on the factors to be considered while establishing supply chain system between farmers and bioenergy companies. The farmers' response was modest due to the limited flexibility with energy crops, reluctance in shifting from food based cropping to energy based cropping, and the lack of confidence in the energy crop market. Farmers require short-term economic gain with long-term agreements from the companies for purchase of energy crops. The local government is directly supporting the project and farmers are getting the bottom ash from the CHP plant and sludge from the waste treatment plants as fertilizer free of cost. The single feedstock system made the energy companies to lease lands from the farmers and develop salix plantations to harvest for their operations without involving farmers directly in the bioenergy production system [53,95]. This approach will lead to the food versus fuel conflict and the 'land grab' issues, and farmers will not get the economic benefit through their active participation in the biorefinery projects.

There are policies in EU to provide subsidies with mandatory blending programs to facilitate the increased use of biofuels with fossil fuels [9]. It is targeted that, by the year 2020, 20% of the energy consumption will be met by renewable energy sources including biofuels. Similarly, the US Energy Security and Independence Act (ESIA) of 2007 is targeted to produce 16 of 21 billion gallons of biofuel produced in 2022 using lignocellulosic materials [31]. Biofuel production is generally not economically competitive with production of fossil fuels at their current market prices and it requires subsidies to promote the utilization of biofuels as energy source [6].

Although some companies are demonstrating lignocellulosic fuel production at pilot scales, commercial viability of this technology is yet to be proven [32]. Some of the major biofuel companies in the United States of America include BlueFire Ethanol, Mascoma Corporation, Verenium Corporation, Pacific Ethanol Inc., and POET. Other major players are Abengoa Bioenergy from Spain, Iogen Corporation and Lignol Energy Corporation in Canada, Inbicon in Denmark, Nippon Oil Corporation in Japan, Praj Industries in India, and SEKAB in Sweden [32]. Some of the major companies producing lignocellulosic ethanol are listed in Table 3. China has been producing cellulosic ethanol since the 1960s. Nancha Wood Hydrolysis Plant in Heilongjiang province had been producing ethanol from woods through acid hydrolysis until 1990 [36]. Henan Tianguan Fuel Ethanol Co., Ltd. has been producing 3000 t bioethanol per year from cellulose since 2006. Similarly, COFCO in Heilongjiang has a capacity to produce 500 t of bioethanol from cellulose. But, the cost of bioethanol is 6000–6500 RMB/t which is higher than corn or wheat based ethanol [33].

Biobased industry is very dynamic, broad and most of its segments are intermingled. About $ 400 billion worth products like chemicals, pulp and paper, fuels, and pharmaceuticals are produced from biomass in USA alone [103]. The important chemicals that can be produced from lignocellulosic biomass are given in Table 4. Present bioeconomy of EU is worth 2 trillion Euros per annum and is providing about 22 million jobs for 9% of the total work force [104]. Major bioproducts derived from lignin fraction of biomass include syngas, Fischer Tropsch liquids, methanol, aromatic acids, vanillin, dimethyl sulphoxide (DMSO), polyelectrolytes, polymer alloys, carbon fibers and composites [105]. The current commercial sale of lignin is mainly as lignosulphonates and some of the companies producing them are Borregaard-LignoTech in Norway, Tembec in Canada, MeadWestvaco (MWV), Georgia-Pacific and LignoTech USA, Inc. in USA. Lignin products have a global market of about 250–300 million dollars [103]. Isolation of lignin in its natural state is difficult as it shows high variation depending on the biomass source. Research and development is required for the practical and economical conversion of natural lignin to chemicals and molecules [105].

Table 3
Examples of biorefineries producing lignocellulosic biofuel.

Company and location	Feedstock(s)	Technology	Bioethanol output capacity	Comments	References
Abengoa, Salamanca, Spain.	Wheat and barley straw	Enzymatic hydrolysis	1.3 million gallons per year	Started production in 2008. Production of 25 million gallons per year is expected by 2014 at Kansas, USA	[63,65]
Beta Renewables, Crescentino, Italy.	*Arundo donax* (Giant reed) and wheat straw	Bio-chemical	20 million gallons per year	Similar capacity plant is expected to start at Sampson County, USA by 2014	[64,65]
Borregaard, Sarpsborg, Norway.	Spruce wood	Thermo-bio-chemical	19 million gallons per year	Operational for more than 40 years Vanillin and lignin are also produced from spruce wood.	[66,96]
Domsjö Fabriker, Örnsköldsvik, Sweden.	Softwood	Bio-chemical	15,000 t per year	Speciality cellulose, lignin and carbonic acid are other main products	[97,98]
Iogen Corporation, Ottawa, Canada.	Agricultural residues	Bio-chemical	6000 l per day	Started demonstration in 2004	[99]
Mascoma, Kinross, Michigan, USA.	Aspen woods	Consolidated Bioprocessing	20 million gallons per year	Expected investment and year of operation are 232 million USD and 2014, respectively	[65,67]
Procéthol 2G Consortium, Pomacle, France.	Wood and agricultural wastes	Bio-chemical	180,000 l per year	Started production in 2010	[100,101]
Sundrop Fuels, Alexandria, Louisiana, USA.	Forest wastes	Methanol-to-Gasoline	50 million gallons per year	Expected investment and year of operation are 500 million USD and 2014, respectively.	[65,102]
KiOR, Natchez, Mississippi, USA.	Yellow pine	Pyrolysis and Fluid catalytic cracking	41 million gallons per year	Expected investment and year of operation are 350 million USD and 2014, respectively.	[65]
Zeachem, Boardman, Oregon, USA.	Hybrid poplar, corn stover and cobs	Bio-chemical	25 million gallons per year	Expected investment and year of operation are 391 million USD and 2014, respectively.	[65,67]

6. Alternate approaches for logistics of lignocellulosic biomass

Production of biofuels and biomaterials from lignocellulosic materials requires primarily the economic analyses of the crop production, biomass harvesting, logistics and storage of the feedstock, pretreatment processes, scale and location of the biorefinery, and distribution of the final products in the market [114]. But, the multitude of drivers and the high potential for production of biofuels and biomaterials do not guarantee the actual benefits for the biomass producers or the farmers especially in the developing countries. Creating a sustainable bioeconomy demands meticulous management at all levels [1]. Advanced and sustainable technologies for the production of biofuels and biomaterials must be transferred to the poor countries by the international institutions. Local institutions must design and manage biomass projects so that farmers will be benefited as biomass producers and consumers of biofuels [115] and biomaterials. The US Senate has passed the Farm Bill 2002, or the Farm Security and Rural Investment Act 2002, recognizing the role to be played by the farmers, foresters and rural communities to achieve the energy security and economic prosperity. It supported the research and development for the development of biorefinery and bioproduct manufacturing [116].

Biorefinery operations also has to follow the characteristics required for any successful project including innovations to meet the people's needs with due consideration to the local environment, utilization of locally available resources mostly on existing capabilities for the self sufficiency, expansion to benefit more people, and people's participation in political and economic development decisions. All stakeholders and the groups that may be negatively affected by the project should be involved in the project development from the start [93]. Fundamental changes in people's thinking and behaviour towards renewable energy along with the development of technologies, methods, and infrastructure are required for the sustainable production and supply of renewable energy to all people [117].

Industrial production of chemicals from biomass can meet the demands for the chemicals which are currently produced from the fossil reserves since the quantity of raw material required is very small when compared to the volume of raw material required for the fuels production. As of 2007, the petroleum used for chemical production in the United States of America was about 3% of the total petroleum consumption, but the value of the chemical products was 375 billion dollars and that of transportation fuels was worth 385 billion dollars which was accounted for about 70% of the total petroleum consumption [70]. The production of chemicals and materials from lignocellulosic biomass by the established industrial chemical producers would be realised if the intermediate chemicals for them can be produced and supplied by the biomass producers. The intermediate products from the farm can be used directly for the production of higher value products without significant additional capital investments [70].

Some of the important steps to overcome the bottlenecks in commercializing biofuel production from lignocellulosic biomass include the utilization of cheaper substrates, cost-effective pretreatment techniques, developing efficient strains of recombinant microorganisms for fuel production, superior product recovery processes, efficient integration of bioprocesses, economic utilization of side products, and the minimization of energy and wastes [32]. It has been shown that, it is not economical to increase the transportation distance of biomass for its value addition. Involvement of local farmers in the logistics of agro residues would help to systematize it by farmers taking care of biomass collection, handling, and transportation in a co-operative manner [32]. Regional disparity in supply and cost of energy can be reduced by decentralized production of it using the local resources with associated income generation and reduction in emission of CO_2 [118]. The life cycle assessment of bioenergy crop production in Japan proved the requirement for improvement in the cultivation technologies and establishment of regional utilization systems to save fossil fuel resources and reducing green house gas emissions. Substitution of petrol by bioethanol produced from bioenergy crops has significant potential to make our society more sustainable [119].

Companies like Archer Daniels Midland (ADM), Deere, and Monsanto has already been looking into the potential of dispersed pretreatment plants to reduce the transportation cost [114]. Atlantic biomass conversions company has developed a technology to produce fermentable sugars through enzymatic treatment on the site of biomass production and transporting these sugars to centralized pretreatment centres to produce biofuels [120].

Table 4
Intermediary chemical products from lignocellulosic biorefineries.

Building block chemical	Chemical derivatives	End uses	References
3-Hydroxypropionic acid ($C_3H_6O_3$)	1,3-Propanediol ($C_3H_8O_2$), acrylic acid ($C_3H_4O_2$), methyl acrylate ($C_4H_6O_2$), acrylamide (C_3H_5NO), acrylonitrile (C_3H_3N), propiolactone ($C_3H_4O_2$), malonic acid ($C_3H_4O_4$)	Biosolvents, biopolymers (e.g., sorona fiber), lubricants, contact lenses, diapers, carpets	[106–108]
Arabitol ($C_5H_{12}O_5$) and xylitol ($C_5H_{12}O_5$)	Xylaric acid ($C_5H_8O_7$), propylene glycol ($C_3H_8O_2$), ethylene glycol ($C_2H_6O_2$), glycerol ($C_3H_8O_3$), lactic acid($C_3H_6O_3$), mixture of hydroxyfurans ($C_5H_{10}O_4$)	Health care products, food additives (e. g., sweeteners), biopolymers (PET analogues), Antifreeze	[106,107]
Bioalcohols (butanol ($C_4H_{10}O$), ethanol (C_2H_6O), methanol (CH_4O), propanol (C_3H_8O)	Acetic acid ($C_2H_4O_2$), acetone(C_3H_6O), acetaldehyde (C_2H_4O), ethyl acetate($C_4H_8O_2$), ethyl chloride(C_2H_5Cl), polyethylene ($(C_2H_4)_n$, formaldehyde(CH_2O), methyl chloride(CH_3Cl), butyl acetate($C_6H_{12}O_2$), ethylene glycol ($C_2H_6O_2$), butyl acrylate ($C_7H_{12}O_2$), isobutene(C_4H_8), paraxylene(C_8H_{10}), butadiene (C_4H_6), propyl acetate ($C_5H_{10}O_2$), propyl iodide (C_3H_7I), chloropropane (C_3H_7Cl), propyl formate($C_4H_8O_2$), propyl ether ($C_6H_{14}O$), propionaldehyde(C_3H_6O), propionic acid ($C_3H_6O_2$)	Biosolvents, biofuels, fuel oxygenates, biopolymers, plasticizer, resins, pharmaceuticals	[103]
Furans (Furfural ($C_5H_4O_2$), Hydroxymethyl furfural ($C_6H_6O_3$), 2,5-Furan dicarboxylic acid ($C_6H_4O_5$))	Succinic acid ($C_4H_6O_4$), 2,5-furandicarbaldehyde ($C_6H_4O_3$), 2,5-bis (aminomethyl)-tetrahydrofuran ($C_6H_{14}N_2O$), 2,5-dihydroxymethyl-furan ($C_6H_8O_3$), 2,5-dihydroxymethyl-tetrahydrofuran ($C_6H_{12}O_3$), levulinic acid ($C_5H_8O_3$), formic acid (CH_2O_2), furfuryl alcohol ($C_5H_6O_2$), tetrahydrofuran (C_4H_8O), diformylfuran ($C_6H_6O_3$)	Biopolymers (e.g., (PET) analogue, nylons), biosolvents	[106,107]
Glycerol ($C_3H_8O_3$)	Glyceric acid ($C_3H_6O_4$), propylene glycol ($C_3H_8O_2$), 1,3-propanediol ($C_3H_8O_2$), glycidol ($C_3H_6O_2$), propanol (C_3H_8O), diglyceraldehyde ($C_6H_{14}O_5$), glycerol carbonate ($C_4H_6O_4$), mono-, di-, or tri- glycerate, branched polyesters and nylons	Biopolymers, pharmaceuticals, antifreeze, Food additives	[106,107]
Isoprene (C_5H_8)	Isoprenol ($C_5H_{10}O$), prenol ($C_5H_{10}O$), squalane ($C_{30}H_{62}$), citral ($C_{10}H_{16}O$), 1,9-nonanediol ($C_9H_{20}O_2$), isopentyldiol ($C_5H_{12}O_2$), Isovaleraldehyde ($C_5H_{10}O$)	Biopolymers (e.g., synthetic rubber), biofuels, pharmaceuticals, fragrances	[107,109,110]
Lactic acid ($C_3H_6O_3$)	Dilactide ($C_6H_8O_4$), lactoyllactic acid ($C_6H_{10}O_5$), calcium stearoyl-2-lactylate ($C_{42}H_{78}CaO_8$), butyl lactate ($C_7H_{14}O_3$), ethyl lactate ($C_5H_{10}O_3$), propyl lactate ($C_6H_{12}O_3$), propylene glycol($C_3H_8O_2$), propylene oxide (C_3H_6O), acrylic acid ($C_3H_4O_2$)	polymers (e.g., polylactic acid (PLA)), food additives, biosolvents, pharmaceuticals	[103,107,111]
Levulinic acid ($C_5H_8O_3$)	1,4-Pentanediol ($C_5H_{12}O_2$), angelilactones ($C_5H_6O_2$), diphenolic acid ($C_{17}H_{18}O_4$), β-acetylacrylic acid ($C_5H_6O_3$), δ-aminolevulinate ($C_5H_9NO_3$), γ-valerolactone ($C_5H_8O_2$), 2-methyl-tetrahydrofuran (C_4H_8O), acrylic acid ($C_3H_4O_2$)	Food additives, biopolymers, pharmaceuticals, pesticides, herbicides, fuel oxygenates	[106]
Sorbitol ($C_6H_{14}O_6$)	Isosorbide ($C_6H_{10}O_4$), propylene glycol ($C_3H_8O_2$), ethylene glycol ($C_2H_6O_2$), glycerol ($C_3H_8O_3$), lactic acid ($C_3H_6O_3$), 2,5-anhydrosugars ($C_6H_{12}O_5$), 1,4-sorbitan ($C_6H_{12}O_5$)	Biosolvents, biopolymers (e.g., polyethylene terephthalate (PET) analogue), antifreeze	[106,112]
Succinic acid ($C_4H_6O_4$)	γ-Butyrolactone ($C_4H_6O_2$), 1,4-butanediol ($C_4H_{10}O_2$), succindiamide ($C_4H_8N_2O_2$), tetrahydrofuran (C_4H_8O), 2-pyrrolidone (C_4H_7NO),1,4-diaminobutane ($C_4H_{12}N_2$), succinonitrile ($C_4H_4N_2$), dibasic ester ($C_6H_{10}O_4$), *N*-methyl pyrrolidone (C_5H_9NO)	Surfactant/detergent, electroplating, food additives, pharmaceuticals, biopolymers, biosolvents	[106,113]

Similarly, the Pure Lignin Environmental Technology, a BC based company has developed a dilute acid fractionation process for lignocellulosic biomass to produce cellulose, lignin, and hemicellulose to be used separately for further value addition [121].

On-farm dilute acid pretreatment of switch grass (*Panicum virgatum* L.) and reed canary grass (*Phalaris arundinacea* L.) was demonstrated to improve the storing and thereafter the simultaneous saccharification and fermentation of them to bioethanol. On-farm wet storage after dilute acid treatment was studied; to increase product uniformity, increase susceptibility to enzymatic hydrolysis, to reduce dry matter loses during storage and to reduce the risk of fire. This study also demonstrated that, on-farm treatment increased the degradability by breaking the bonds between the polymeric components of the feedstock while it was under anaerobic storage conditions. The treatment also increased the stability of the treated material by reducing the microbial attack on it. Finally it would reduce the intensity of treatments required at the industry and thus provide higher income to the farmers for the value added feedstock [122].

Decentralized small and medium sized combined heat and power plants using regionally available feedstocks has been suggested as a method to generate electricity [39] and rural jobs in the agricultural counties of Taiwan [94]. It is been shown that smaller sized biorefineries will decrease the overall supply chain costs by reducing the transportation costs. It is estimated that in the price of the lignocellulosic ethanol, 49% is due to investment cost, 21% is due to operational cost, 10% is due to feedstock collection cost, 3% is inventory cost, and 17% is due to transportation cost. So, the biomass which is highly available in the nearby areas should be used for the biorefinery to reduce the price of the final product to as minimum as possible [57]. The energy requirement for biorefinery operations can be minimized by utilizing the geothermal energy wherever it is available. This would improve the resource utilization efficiency and also it will help in economical production of electricity from biomass [123].

Farm-scale biorefinery to produce animal feed, bioethanol, biofertilizer and biogas has been investigated in an organic farm in Denmark and was shown to be a sustainable practice that helps in decreasing the fossil fuel use and increases the economic performances of the organic farming [124]. The decentralized combined heat and power (CHP) plants are increasing in Finland, Denmark, Sweden, Austria, and South Tyrol region in Northern Italy. In Austria, 266 CHP plants for district heating were operational in 1995 with an annual growth rate of about 10%. Swedish biomass utilization for district power production was aimed to reach 58 PJ/year by 2000 [125]. Similar to the decentralized production of power and heat in several European countries, decentralized biomass processing for centralized biorefinery operations can be developed for both the developing and developed countries.

The rapid and unmanageable urban growth to some extent can be attributed to the higher availability of energy in urban areas

than in rural areas. Provision for uninterrupted energy in rural areas can control the people migration to urban areas to some extent. Various forms of decentralized energy resources [118] and energy cooperatives with additional measures for the sustainable forestry management and biofuel initiatives would improve the rural living standards [14]. Dependence on fossil resources for biorefinery operations can be reduced by utilizing locally available resources such as biofertilizers and residues of agriculture and industry. The end products should find users in the vicinity of the industry itself [84].

More research is required on the development of sustainable supply chain management especially for the supply of biomass for biorefinery operations. Enabling sustainable supply chain management requires the consideration of environmental and social benefits in addition to the economical benefits [59]. The life cycle analysis based standards can be implemented throughout the supply chain for the environmental [126] and social performance of the supply chain system [127]. Life cycle analysis (LCA) methods evaluate technologies, processes and products so as to determine their requirements, impacts, inclination to consume resources and generate pollution. Impacts of biorefinery operations on climate, water resources, land, nutrient cycle, human and health would be studied in LCA. Economic and social impacts would also be considered by the LCA practitioners [13,128]. LCA analyses also shown that, utilization of agricultural residues requires the best management practises with carefully standardised harvest rates. The quantity of crop residue that can be removed from the field, without affecting the soil carbon, for biorefinery operations depends on crop rotation, tillage practises, fertilization management, soil properties, and climate [34].

7. The approach of decentralized pretreatment and centralized biorefinery

Decentralized biomass processing concept such as 'rural biorefinery' is defined as an integrated factory to produce value added materials from crops which is located in the middle of a farming community. In this model concept, the whole crop will be harvested, stored and then fractionated into products and by-products for sale [129]. Rural biorefinery processing whole wheat crop to flour, bran, fibre, straw meal, and residues is shown as profitable [130]. Carolan et al. [5] had proposed the concept of regional biomass processing centres (RBPC), which is a network of biomass supply chain for the operation of a biorefinery by processing biomass into various intermediary products for the production of fuels, chemicals, electricity and animal feeds [5]. The concept of Regional Biomass Processing Depots (RBPDs) has been emphasised by many researchers in order to address the issues associated with the biomass logistics. The problems such as low bulk density of the feedstock, compositional and seasonal variability of the biomass, and regional environmental issues would be addressed in the RBPD concept. In general, RBPDs are used to pretreat and densify biomass at distributed facilities to be transported to the distant biorefinery [131]. Densification of the feedstock will significantly reduce the traffic congestion resulting from the additional biomass supply process [132]. These types of depots are currently being studied for aggregation, storage, size reduction and densification of switchgrass and corn cobs by the Tennessee Biomass Supply Co-operative which is part of the University of Tennessee Biofuels Initiative. The densified biomass will then be transported to a biorefinery operated by DuPont-Danisco Cellulosic Ethanol (DDCE). Similar concept is also studied by Idaho National Laboratory (INL) under their bioenergy program to supply feedstock in uniform format using same type of biomass. The RBPDs aim to provide rural employment and wealth through establishing low capital biomass processing facilities owned by the community to process the feedstock produced by the regional farmers. It also aimed to process the feedstock into intermediate products for the production of animal feeds and other biomaterials. The pretreatment process for a RBPD should be of low cost and simple that can be used produce stable intermediate products and valuable co-products. The potential processes include dilute acid [122], hot water, steam explosion, lime, and treatments using ammonia like ammonia recycle percolation (ARP) and ammonia fiber expansion (AFEX). AFEX would be particularly suitable for RBPD as the product after treatment can be briquetted easily as it contains the liberated lignin which act as a natural adhesive [133]. However, the techno-economic modeling studies pointed to the requirement of further research to improve the profitability of biomass processing in local biomass processing depots [131].

The high transportation cost makes it difficult for the economical production of biofuels and biomaterials from low density lignocellulosic biomass. Present system of smaller 50 to 100 million gallons per year biorefineries utilizes only a single type of crop grown in the economical transportation range of about 50 to 75 miles. The actual available area in this range of 50 to 75 miles particularly for the cultivation of the selected crop will vary from region to region and the required capacity of the biorefineries should be 2–5 billion gallons per year to meet the need for biofuels and biomaterials. The decentralized pretreatment of lignocellulosic raw materials at their site of production itself [88] to the precursors of biofuels and biomaterials followed by their transportation to centralized refineries for their final conversions to fuels and materials will increase the availability of raw materials in their economical transportation range and thereby increase the production capacities for biorefineries. Examples for the precursors of biofuels and biomaterials are; soluble sugars, cellulose, hemicellulose, lignin, minerals, volatiles, bio-oil, biochar, torrefied biomass pellets, etc., which are produced from biomass through thermochemical pretreatment processes. Liquefaction of biomass will enable the transportation of it through pipelines and trucks and also across the continents in ships similar to the current transport of petroleum. There are multiple benefits of this approach to both the biomass producers and the industries. Farmers can cultivate the economically advantageous crop in their fields and convert it or the residues to the precursors of biofuels and biomaterials. Decentralized biomass pretreatment will generate new job opportunities and infrastructural developments especially in rural areas where biomass is produced. Biorefineries will receive the precursors for their operations on an year-round basis and thereby making the production of biofuels and biomaterials economical thus inviting more investments for the industry [134]. The precursors from the decentralized pretreatments will be pure, dense, and specific for particular biorefinery operations and thus the pretreatment and detoxification can be avoided from the biorefineries [4]. The concept of decentralized biomass processing and centralized biorefinery operations is depicted in Fig. 2. The biomass produced in the farm community would be processed at the decentralized processing centres and the processed materials would be supplied to different final processing industries including the biorefinery. The finished products from the industries would be supplied in the market including those in the farming communities. The minerals from the biomass would be directly used as fertilizer in the farm and the bioenergy produced at the biorefinery would be used for their operations before selling the surplus energy to the market.

The decentralized pretreatment has some problems for commercial implementation. Storage of biomass at different locations would result in compounded mass loss and the processes such as size reduction and densification are energy intensive. If the facility is intended to use for a single type of feedstock, it would result in under usage of the

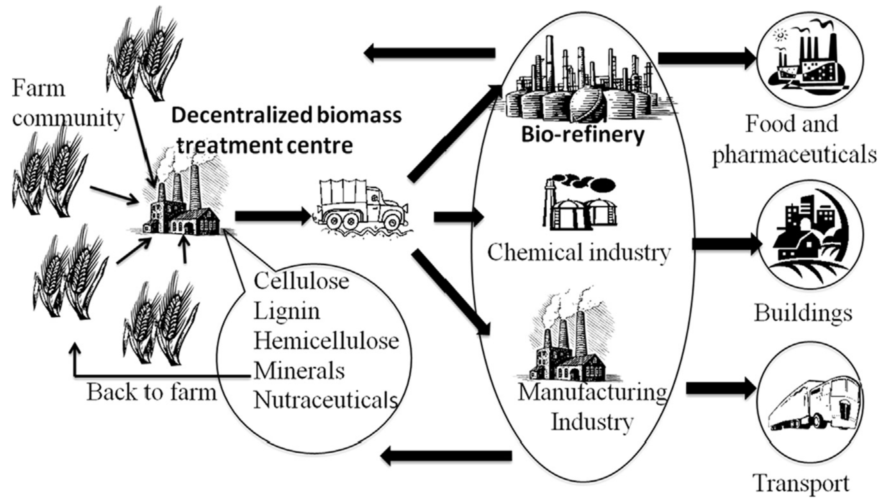

Fig. 2. The concept of decentralized biomass pretreatment and centralized biorefinery.

equipments and the small scale of operation would have its disadvantages in terms of economics. The mass loss due to microbial contamination has to be prevented during storage and transport. Similarly, mass loss would be occur during size reduction and the combined loss from size reduction, storage and transport is estimated to be about 10–15% resulting in significant loss of income. RBPDs placed along the rail lines would be more economical than transportation on road using trucks. The scale of operation should also be economical and co-operative mode of operation among farmers would achieve the minimum required scale of operation probably in the range of 100–1000 t/day. Seasonal variation in biomass availability also has to be addressed in an RBPD by having facilities for handling of multiple feedstocks and different processes and technologies for multiple products. The energy requirement for size reduction and densification has to be reduced for additional advantages in the feedstock logistics. The life cycle analysis study of the decentralized pretreatment and transportation of the feedstock for centralized biorefinery showed that it has same energy efficiency as that of a centralized pretreatment at the biorefinery but with reduced green house gas emissions [133].

8. Conclusion

There is a lot of scope for scientific, technical and engineering developments to realize the concept of sustainable biorefineries. Utilization of agricultural residues for the biorefinery operations will provide additional income to the farmers and would also create rural employment opportunities. Multipurpose bioenergy crops like sweet sorghum would provide food, fodder and fuel in arid and semi-arid areas of the world. Algae can be cultivated in brackish and waste waters and can be used to control the release of green house gases to the atmosphere. Availability of municipal solid wastes (MSW) is increasing year by year and is a potential resource for biorefinery operations. Ongoing research activities are expected to come up with the development of sustainable supply chain systems for agricultural and other resources for biorefineries. Integrated biorefineries would process the bioresources to produce fuel and materials which are produced in the current petroleum based refineries. Studies have shown that it may take another 10 years or so for the commercial production of biofuels and biomaterials. Regional processing of the raw materials for centralized biorefinery operations will provide additional job and income to the farmers in rural areas. It would provide continuous and sustainable supply of raw materials to the biorefineries for the production of biofuels and biomaterials.

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